

Kondo Effect of a Jahn-Teller Ion Vibrating in a Cubic Anharmonic Potential

Takashi Hotta

Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

(Received May 30, 2014)

We discuss the Kondo effect in a spinless two-orbital conduction electron system coupled with anharmonic Jahn-Teller vibration by employing a numerical renormalization group technique. When a temperature T is decreased, we encounter a plateau of $\log 3$ entropy due to quasi-triple degeneracy of local low-energy states, composed of vibronic ground states and the first excited state with an excitation energy of ΔE . Around at $T \approx \Delta E$, we observe an entropy change from $\log 3$ to $\log 2$. This $\log 2$ entropy originates from the rotational degree of freedom of the vibronic state and it is eventually released due to the screening by orbital moments of conduction electrons, leading to the Kondo effect of a Jahn-Teller ion. The Kondo temperature is explained by the effective s - d model with anisotropic exchange interactions.

KEYWORDS: Kondo effect, Dynamical Jahn-Teller effect, Vibronic state, Cubic anharmonicity

1. Introduction

One of recent trends in the research field of condensed matter physics is to explore exotic magnetism and unconventional superconductivity in heavy-electron materials.^{1,2)} Concerning the emergence of heavy-electron state, a traditional mechanism is based upon quantum criticality induced by the competition between the Kondo effect and Ruderman-Kittel-Kasuya-Yosida interaction. The Kondo effect due to local magnetic moment has been well understood,³⁾ but it is recognized that the Kondo-like phenomenon should occur in more general, when a localized entity with internal degrees of freedom is embedded in a conduction electron system and quantum-mechanical exchange interaction effectively works between local degrees of freedom and conduction electrons.

In particular, a possibility of Kondo phenomenon with phonon origin has been pointed out by Jun Kondo himself in a conduction electron system coupled with a local double-well potential.^{4,5)} The Kondo effect in such a two-level system has been discussed actively by several groups.⁶⁻¹¹⁾ Recently, the research of the phononic Kondo effect has revived due to active experimental investigations on cage-structure compounds in which a guest atom is contained in a cage composed of relatively light atoms and it oscillates with large amplitude in a potential with strong anharmonicity. Such local oscillation with large amplitude is called rattling and exotic phenomena induced by rattling have attracted much attention in the research of strongly correlated electron materials with cage structure.¹²⁾

Among them, magnetically robust heavy-electron state has been vigorously investigated both from experimental and theoretical sides.¹³⁻³⁵⁾ The non-magnetic Kondo effect with phonon origin has been discussed for the purpose to understand peculiar magnetically robust heavy-electron state. In these theoretical investigations, anharmonic Holstein phonon has been frequently discussed, but it is possible to bring rich physics when we consider Jahn-Teller vibration of rattling in cage materials. In fact, when Jahn-Teller phonons are dynamically coupled with orbital degree of freedom of electrons, the local ground state is known to be a vibronic state characterized by clockwise and anti-clockwise rotational mode of Jahn-Teller phonons.^{19,20,22)} Such chiral degree of freedom

is screened by orbital moments of conduction electrons and there occurs the release of an entropy $\log 2$ of the vibronic state, leading to the Kondo-like phenomenon.

Although the effect of a weak anharmonicity has been partly considered by the present author to confirm the relation between the Kondo temperature and the static Jahn-Teller energy,¹⁹⁾ previous research has been done mainly for the harmonic potential of Jahn-Teller ion in order to focus on the Kondo effect due to chiral degree of freedom of vibronic state. Here we have an interest on the effect of strong anharmonicity in the potential for Jahn-Teller ion. It has been well known that three potential minima appears when cubic anharmonicity is included in the potential for Jahn-Teller ion. In particular, it is worth to investigate the competition between the positional degree of freedom of three potential minima and the chiral degree of freedom of vibronic state.

In this paper, we numerically analyze the Jahn-Teller-Anderson model including the coupling between conduction electrons and anharmonic Jahn-Teller phonons on an impurity site. For the convenience of the calculation, we introduce unitary transformations of electron and phonon operators, which naturally express the rotational mode of Jahn-Teller phonons. By using a numerical renormalization group method, we evaluate entropy, specific heat, and several kinds of susceptibilities. It is found that the magnitude of entropy changes in the order of $\log 3$, $\log 2$, and 0, when we decrease a temperature. The appearance of $\log 3$ entropy originates from quasi-triple degeneracy of local low-energy states, composed of vibronic ground states and the first excited state. The entropy of $\log 2$ is due to the double degeneracy of the vibronic ground state composed of electron and dynamical Jahn-Teller vibration. We discuss the origin of the temperature at which entropy changes from $\log 3$ to $\log 2$ in addition to the Kondo temperature T_K corresponding to the entropy release of $\log 2$. We attempt to explain the behavior of T_K by introducing the effective s - d model from the original Hamiltonian.

The organization of this paper is as follows. In Sec. 2, we explain the properties of local phonon and vibronic states. In particular, we focus on the local vibronic ground state and the first excited state. In Sec. 3, we introduce the Jahn-Teller-Anderson model to discuss the Kondo phenomenon. We also briefly explain the method used in this paper and define sev-

eral kinds of susceptibilities. In Sec. 4, we exhibit our numerical results and discuss how an entropy changes with the decrease of a temperature. Then, we clarify the energy scale for the entropy release from $\log 3$ to $\log 2$ as well as the Kondo temperature corresponding to the entropy release of $\log 2$. We also introduce the effective s - d model to discuss the behavior of T_K . Finally, in Sec. 5, we provide a few comments on related future problems and summarize this paper. Throughout this paper, we use such units as $\hbar=k_B=1$.

2. Local Phonon and Vibronic States

2.1 Anharmonic Potential

First let us consider the Jahn-Teller oscillation in an anharmonic potential. The Hamiltonian is given by

$$H_{\text{ph}} = \frac{1}{2M}(P_2^2 + P_3^2) + V(Q_2, Q_3), \quad (1)$$

where M is the reduced mass of Jahn-Teller oscillator, Q_2 and Q_3 denote normal coordinates of $(x^2 - y^2)$ - and $(3z^2 - r^2)$ -type Jahn-Teller oscillation, respectively, P_2 and P_3 indicate corresponding canonical momenta, and $V(Q_2, Q_3)$ is the potential for the Jahn-Teller oscillator. Here we do not use Q_1 , since it usually indicates breathing-mode oscillation, which is ignored in this paper. Then, the potential is given by

$$V(Q_2, Q_3) = A(Q_2^2 + Q_3^2) + B(Q_3^3 - 3Q_2^2Q_3) + C(Q_2^2 + Q_3^2)^2, \quad (2)$$

where A indicates the quadratic term of the potential, while B and C are, respectively, the coefficients for third- and fourth-order anharmonic terms. Note that we consider only the anharmonicity which maintains the cubic symmetry. Here we consider the case of $A>0$ and $C>0$, while B takes both positive and negative values.

Before proceeding to the quantization, we briefly explain the properties of the potential. For the purpose, it is convenient to introduce the non-dimensional distortion as $q_2=Q_2/\ell$ and $q_3=Q_3/\ell$, where ℓ denotes the amplitude of the zero-point oscillation, given by $\ell=1/\sqrt{2M\omega}$ and ω is the phonon energy given by $\omega=\sqrt{2A/M}$. With the use of q_2 and q_3 , we express V in the unit of ω as

$$V(q_2, q_3) = \omega \left[\frac{1}{4}(q_2^2 + q_3^2) + \frac{\beta}{3}(q_3^3 - 3q_2^2q_3) + \frac{\gamma}{8}(q_2^2 + q_3^2)^2 \right], \quad (3)$$

where β and γ are non-dimensional anharmonicity parameters, defined by

$$\beta = \frac{3B}{(2M)^{3/2}\omega^{5/2}}, \gamma = \frac{2C}{M^2\omega^3}. \quad (4)$$

By introducing further q and θ through the relations of $q_3=q \cos \theta$ and $q_2=q \sin \theta$, we rewritten V as

$$V(q, \theta) = \omega \left(\frac{q^2}{4} + \frac{\beta q^3 \cos 3\theta}{3} + \frac{\gamma q^4}{8} \right). \quad (5)$$

For $|\beta| \leq \sqrt{\gamma}$, there exists a single minimum at $q=0$, while for $|\beta| > \sqrt{\gamma}$, there appear three minima for $q \neq 0$ in addition to the shallow minimum at $q=0$.

In Fig. 1, we show the contour plot of the potential V on the q_3 - q_2 plane for $\gamma=1$. Figure 1(a) denotes the case of $\beta=0$. The fourth-order anharmonicity is included, but the potential min-

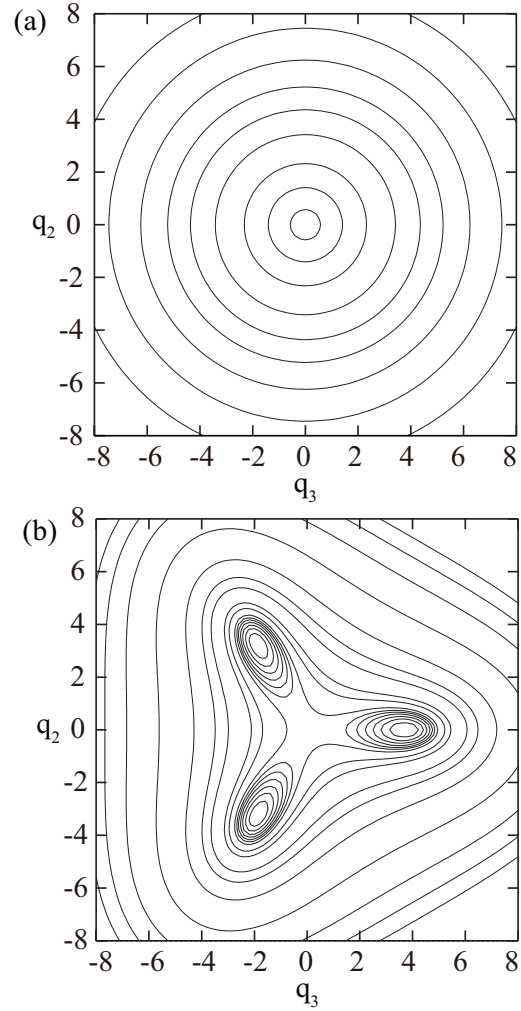


Fig. 1. Contour plot of $V(q_2, q_3)/\omega$ on the q_3 - q_2 plane for (a) $\beta=0$ and (b) $\beta=-2$. Here we set $\gamma=1$. For the case of (a), we draw the contour curves for $V(q_2, q_3)/\omega=0.1, 1, 5, 20, 50, 100, 200, 400$, and 800 , while for (b), we plot the contours for $V(q_2, q_3)/\omega=-6, -5, -4, -3, -2, -1, 0.5, 5, 10, 30, 50, 100, 250, 500$, and 750 .

imum still appears at the origin. The increase of the potential for large q_2 and q_3 becomes rapid, but there is no significant difference in comparison with the harmonic case of $\beta=\gamma=0$. In Fig. 1(b), we show the case of $\beta=-2$, in which we clearly observe the cubic symmetry in the q_3 - q_2 plane due to the third-order anharmonicity, instead of the rotational symmetry for the case of $\beta=0$. At the present case with $\beta=-2$, we find three minima along the directions of $\theta=0, 2\pi/3$, and $4\pi/3$, corresponding to $(3z^2 - r^2)$ -, $(3x^2 - r^2)$ -, and $(3y^2 - r^2)$ -type Jahn-Teller distortions, respectively.

2.2 Phonon State

In order to discuss the local phonon states, it is necessary to perform the quantization procedure through the relations of $q_2=a_2 + a_2^\dagger$ and $q_3=a_3 + a_3^\dagger$, where a_2 and a_3 are annihilation operators of phonons for Jahn-Teller oscillations. Then, the Hamiltonian is rewritten as

$$H_{\text{ph}} = \omega(a_2^\dagger a_2 + a_3^\dagger a_3 + 1) + (\omega\beta/3)[(a_3 + a_3^\dagger)^3 - 3(a_2 + a_2^\dagger)^2(a_3 + a_3^\dagger)] \quad (6)$$

It is possible to diagonalize this Hamiltonian H_{ph} , but in order to clarify the conserved quantities in the dynamical Jahn-Teller oscillation, it is useful to introduce the following transformation for phonon operators:³⁶⁾

$$a_{\pm} = (a_3 \pm ia_2)/\sqrt{2}, \quad (7)$$

where the sign in this equation is intuitively understood as the rotational direction in the potential. As shown below, in these bases, it is easy to classify the eigenstates by the symmetry of the Hamiltonian. In a numerical renormalization group method, it is quite useful to label the eigenstates with the use of conserved quantities to keep the precision with the limited number of the state.

With the use of these operators, after some algebraic calculations, the Hamiltonian is rewritten as

$$\begin{aligned} H_{\text{ph}} = & \omega(a_+^\dagger a_+ + a_-^\dagger a_- + 1) \\ & + \frac{\omega\beta}{3}[(a_+ + a_-^\dagger)^3 + (a_- + a_+^\dagger)^3] \\ & + \frac{\omega\gamma}{2}(a_+^\dagger a_+ + a_-^\dagger a_- + 1 + a_+^\dagger a_-^\dagger + a_+ a_-)^2. \end{aligned} \quad (8)$$

When we diagonalize this Hamiltonian, we use the phonon basis expressed by $|L; n\rangle$, where L has a physical meaning of angular momentum, while n indicates the phonon number. Explicitly we define them as

$$|L; n\rangle = \begin{cases} |L + n, n\rangle & L \geq 0 \\ |n, n + |L|| & L < 0, \end{cases} \quad (9)$$

where the phonon basis $|n_+, n_-\rangle$ is defined by

$$|n_+, n_-\rangle = \frac{1}{\sqrt{n_+!n_-!}}(a_+^\dagger)^{n_+}(a_-^\dagger)^{n_-}|0\rangle. \quad (10)$$

For the case of $\beta=0$, the phonon state is labelled by the angular momentum L , of which operator is given by

$$L = a_+^\dagger a_+ - a_-^\dagger a_-. \quad (11)$$

Note that L commutes with H_{ph} for $\beta=0$. Thus, when we diagonalize the Hamiltonian for $\beta=0$, we prepare the phonon basis for a fixed value of L , since the states with different L are not mixed. The physical meaning of L is clear. When the potential has continuous rotational symmetry for $\beta=0$, the angular momentum should be the conserved quantity in the quantum mechanics.

However, when we include the effect of β , namely, cubic anharmonicity, the situation is changed. As easily understood from eq. (5), there occurs a trigonal term in the potential and in such a case, L is not the good quantum number, but there still exists conserved quantity concerning L . In order to clarify this point, we express L as

$$L = 3\ell + L_0, \quad (12)$$

where L_0 takes the values of 0 and ± 1 . We find that L_0 becomes the conserved quantity for $\beta \neq 0$. Thus, the local phonon state is expressed as

$$|\Phi_{k,L_0}^{(0)}\rangle = \sum_{\ell,n} P_{\ell,n}^{(k,L_0)} |3\ell + L_0; n\rangle, \quad (13)$$

where $|\Phi_{k,L_0}^{(N)}\rangle$ denotes the k -th eigenstate of H_{ph} characterized by quantum number L_0 , N denotes electron number, and P is the coefficient of the eigenstates. The correspond-

ing eigenenergy is expressed by $E_{k,L_0}^{(N)}$.

Note that for the case of $L_0=0$, there exists extra conserved quantity, which is a parity concerning the change of $\ell \rightarrow -\ell$. It is understood from the fact that the bonding and anti-bonding states of $|3\ell; n\rangle$ and $|-3\ell; n\rangle$ are not mixed with each other. Then, the parity for the bonding (even) or anti-bonding (odd) state is another good quantum number. When we pursue the properties of phonon states more precisely, it is important to consider the parity. However, such discussion is meaningful in the high-temperature region and we do not mention it anymore in the present paper, since we are interested in the low-temperature properties of the Kondo phenomena. The peculiar properties of anharmonic Jahn-Teller vibration in the high-temperature region will be discussed in a separate paper in the near future.

2.3 Vibronic State

Next we consider the electron-phonon coupled state. For the purpose, we calculate the eigenstate of H_{loc} , given by

$$H_{\text{loc}} = H_{\text{el-ph}} + H_{\text{ph}}. \quad (14)$$

Here $H_{\text{el-ph}}$ denotes the electron-phonon coupling term, given by

$$H_{\text{el-ph}} = g(\tau_x Q_2 + \tau_z Q_3), \quad (15)$$

where $\tau_x = d_a^\dagger d_b + d_b^\dagger d_a$, $\tau_z = d_a^\dagger d_z - d_b^\dagger d_b$, d_τ is the annihilation operator of spinless fermion with orbital τ , a and b correspond to $x^2 - y^2$ and $3z^2 - r^2$ orbitals, respectively, and g is the electron-phonon coupling constant. In accordance with the transformation of phonon operator, we introduce the pseudo-spin expression for electron operators as

$$d_\sigma = (d_a \pm id_b)/\sqrt{2}, \quad (16)$$

where σ denotes a pseudospin and \uparrow (\downarrow) corresponds to $+$ ($-$) sign. Then, we obtain

$$H_{\text{el-ph}} = \sqrt{2}\alpha\omega[(a_+ + a_-^\dagger)\sigma_+ + (a_- + a_+^\dagger)\sigma_-], \quad (17)$$

where α is the non-dimensional electron-phonon coupling constant, given by $\alpha = g^2/(2M\omega^3)$, $\sigma_+ = d_\uparrow^\dagger d_\downarrow$, and $\sigma_- = d_\downarrow^\dagger d_\uparrow$. In this paper, we consider the case of half-filling, in which average electron number at an impurity site is unity. Thus, the local ground state is found in the one-electron sector of H_{loc} .

For the harmonic Jahn-Teller phonons with $\beta=\gamma=0$, we find the vibronic ground state with double degeneracy, characterized by the total angular momentum J ,³⁶⁾ given by

$$J = L + \sigma_z/2, \quad (18)$$

where σ_z denotes the z -component of pseudospin, given by $\sigma_z = d_\uparrow^\dagger d_\uparrow - d_\downarrow^\dagger d_\downarrow$. With the use of J , we express the eigenstate as

$$\begin{aligned} |\Phi_{k,J}^{(1)}\rangle = & \sum_n [Q_n^{(k,J)} d_\uparrow^\dagger |J - 1/2; n\rangle \\ & + R_n^{(k,J)} d_\downarrow^\dagger |J + 1/2; n\rangle], \end{aligned} \quad (19)$$

where J takes half-odd-integer value as $J = \pm 1/2, \pm 3/2, \dots$. The double degeneracy in the ground states with $J = \pm 1/2$ originates from clockwise and anti-clockwise rotational directions of vibronic states.

When we include the cubic anharmonicity, J is not the good quantum number, but there still exists a label of to-

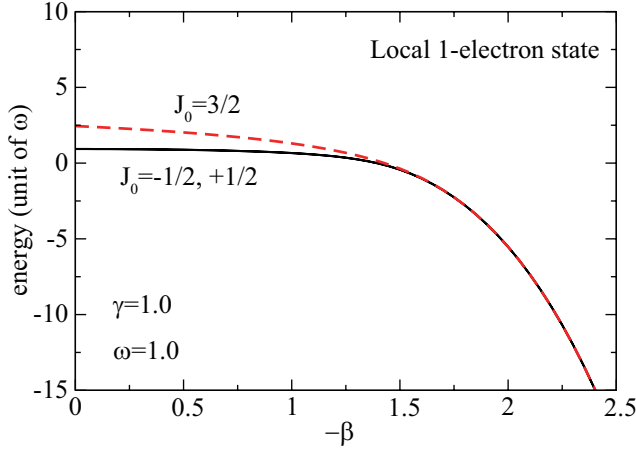


Fig. 2. Eigenenergies vs. $-\beta$ for the states of $J_0 = \pm 1/2$ and $3/2$.

tal angular momentum $J_0 = L_0 + 1/2$ to specify the eigenstate. Since L_0 takes 0 and ± 1 , J_0 becomes $\pm 1/2$ and $\pm 3/2$. Note, however, that the state with $J_0 = -3/2$ belongs to the same group as $J_0 = 3/2$, since $J_0 = -3/2$ is equal to $J_0 = 3/2$ when we add three, as understood from eq. (12). Then, we obtain three groups for the vibronic states characterized by $J_0 = +1/2, -1/2$, and $3/2$. Explicitly, they are expressed as

$$|\Phi_{k,+1/2}^{(1)}\rangle = \sum_{\ell,n} [Q_{\ell,n}^{(k,1/2)} d_{\uparrow}^{\dagger} |3\ell; n\rangle + R_{\ell,n}^{(k,1/2)} d_{\downarrow}^{\dagger} |3\ell + 1; n\rangle], \quad (20)$$

$$|\Phi_{k,-1/2}^{(1)}\rangle = \sum_{\ell,n} [Q_{\ell,n}^{(k,-1/2)} d_{\uparrow}^{\dagger} |3\ell - 1; n\rangle + R_{\ell,n}^{(k,-1/2)} d_{\downarrow}^{\dagger} |3\ell; n\rangle], \quad (21)$$

and

$$|\Phi_{k,3/2}^{(1)}\rangle = \sum_{\ell,n} [Q_{\ell,n}^{(k,3/2)} d_{\uparrow}^{\dagger} |3\ell + 1; n\rangle + R_{\ell,n}^{(k,3/2)} d_{\downarrow}^{\dagger} |3\ell - 1; n\rangle], \quad (22)$$

respectively.

In Fig. 2, we show the corresponding eigenenergies of $E_{0,J_0}^{(1)}$ as functions of $-\beta$ for $\gamma=1$. It is observed that the ground state has still double degeneracy, characterized by $J_0 = \pm 1/2$, even when we consider the cubic anharmonicity. The state with $J_0 = 3/2$ is the excited state, but $E_{0,3/2}^{(1)}$ seems to be almost equal to $E_{0,\pm 1/2}^{(1)}$ in the region of $-\beta > 1.5$. The excitation energy becomes exponentially small for large $|\beta|$. This quasi degeneracy is understood as follows: The potential minima become deep and the quantum tunneling motion is suppressed, when $|\beta|$ is increased. Thus, the energy difference due to rotational motion becomes very small.

For the case of $N=2$ with double occupancy, the coupling between electrons and Jahn-Teller vibration becomes inactive. Then, the eigenstate is written as

$$|\Phi_{k,L_0}^{(2)}\rangle = \sum_{\ell,n} P_{\ell,n}^{(k,L_0)} d_{\uparrow}^{\dagger} d_{\downarrow}^{\dagger} |3\ell + L_0; n\rangle, \quad (23)$$

where the coefficient P is the same as that of $|\Phi_{k,J}^{(0)}\rangle$.

3. Model and Method

Now we consider the conduction electron hybridized with localized electrons. Then, the model is expressed as

$$H = \sum_{\mathbf{k}\tau} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\tau}^{\dagger} c_{\mathbf{k}\tau} + \sum_{\mathbf{k}\tau} (V c_{\mathbf{k}\tau}^{\dagger} d_{\tau} + \text{h.c.}) + H_{\text{loc}}, \quad (24)$$

where $\varepsilon_{\mathbf{k}}$ is the dispersion of conduction electron, $c_{\mathbf{k}\tau}$ is an annihilation operator of conduction electron with momentum \mathbf{k} and orbital τ , and V is the hybridization between conduction and localized electrons. The energy unit is a half of the conduction bandwidth, D , which is set as unity in the following.

In order to investigate electronic and phononic properties of H at low temperatures, we usually discuss corresponding susceptibilities. The susceptibility of an arbitrary operator A is expressed by

$$\chi_A = \frac{1}{Z} \sum_{n,m} \frac{e^{-E_n/T} - e^{-E_m/T}}{E_m - E_n} |\langle m|A|n\rangle|^2, \quad (25)$$

where E_n is the eigenenergy for the n -th eigenstate $|n\rangle$ of H and Z is the partition function given by $Z = \sum_n e^{-E_n/T}$.

For the evaluation of susceptibilities, here we employ a numerical renormalization group (NRG) method,^{37,38)} in which momentum space is logarithmically discretized to include efficiently the conduction electrons near the Fermi energy and the conduction electron states are characterized by “shell” labeled by N . The shell of $N=0$ denotes an impurity site described by the local Hamiltonian. The Hamiltonian is transformed into the recursion form as

$$H_{N+1} = \sqrt{\Lambda} H_N + t_N \sum_{\sigma} (c_{N\sigma}^{\dagger} c_{N+1\sigma} + c_{N+1\sigma}^{\dagger} c_{N\sigma}), \quad (26)$$

where Λ is a parameter for logarithmic discretization, $c_{N\sigma}$ denotes the annihilation operator of conduction electron in the N -shell, and t_N indicates “hopping” of electron between N - and $(N+1)$ -shells, expressed by

$$t_N = \frac{(1 + \Lambda^{-1})(1 - \Lambda^{-N-1})}{2\sqrt{(1 - \Lambda^{-2N-1})(1 - \Lambda^{-2N-3})}}. \quad (27)$$

The initial term H_0 is given by

$$H_0 = \Lambda^{-1/2} [H_{\text{loc}} + \sum_{\sigma} V (c_{0\sigma}^{\dagger} d_{\sigma} + d_{\sigma}^{\dagger} c_{0\sigma})]. \quad (28)$$

We also evaluate entropy and specific heat of localized electron. In the NRG calculations, a temperature T is defined as $T = \Lambda^{-(N-1)/2}$. In this paper, we set $\Lambda=5$ and we keep $M=5000$ low-energy states for each renormalization step. The phonon basis $|L; n\rangle$ of eq. (9) is truncated at a finite number N_{ph} and a maximum angular momentum L_{max} . In order to check the convergence of the results, we have performed the numerical calculations for N_{ph} and L_{max} up to 120 and 60, respectively.

4. Calculated Results

Now we move on to NRG results of the anharmonic Jahn-Teller-Anderson model. In Fig. 3(a), we show the results of entropy and specific heat. In a high-temperature region, an entropy is rapidly decreased with the decrease of a temperature T and it forms a plateau of $\log 3$ between $10^{-5} < T < 10^{-2}$. The origin of $\log 3$ entropy is the quasi-degeneracy of lo-

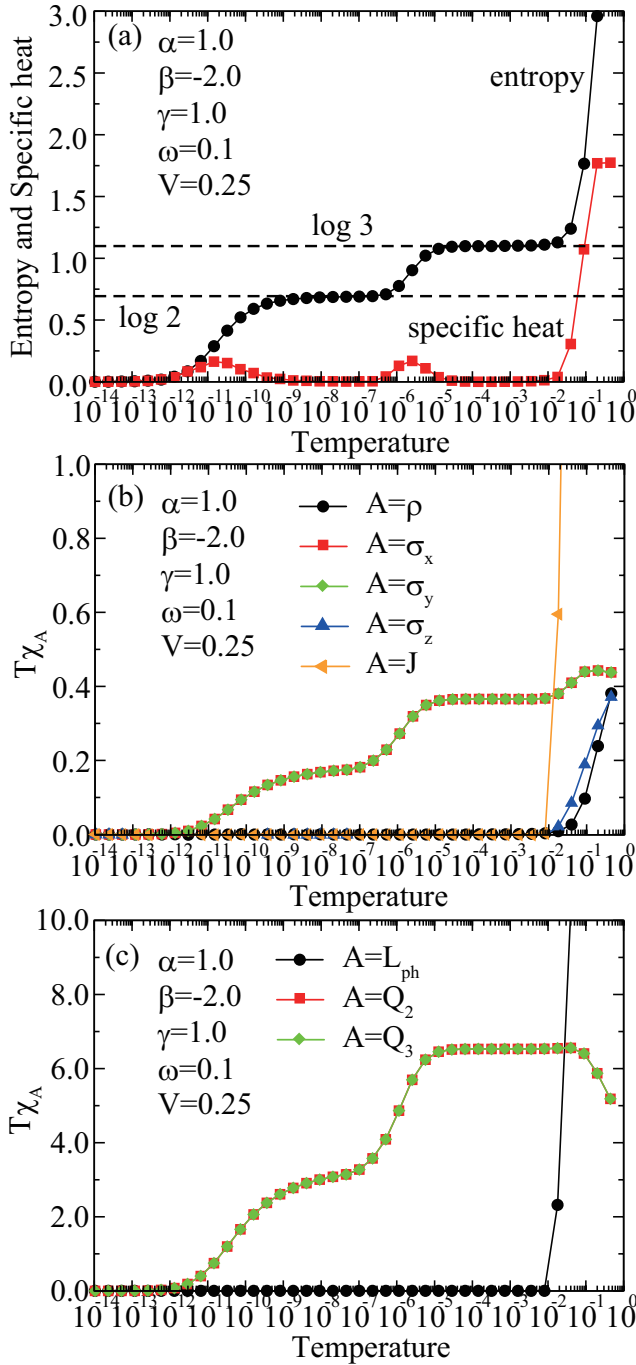


Fig. 3. (a) Entropy and specific heat for $\omega=0.1$, $\alpha=1$, $\beta=-2$, and $\gamma=1$. (a) Susceptibilities for charge, pseudospin, and total angular momentum for the same parameters as in (a). (c) Susceptibilities for phonon rotational moment and Jahn-Teller vibration Q_2 and Q_3 for the same parameters as in (a).

cal low-energy states. As mentioned in Sec. 2, for the one-electron case, we find the vibronic ground states characterized by $J_0=\pm 1/2$ with double degeneracy and the first excited state characterized by $J_0=3/2$. As already shown in Fig. 2, we always obtain the vibronic ground states, but the excitation energy ΔE becomes exponentially small for large $|\beta|$ such as $\beta=-2$. Thus, we observe the log 3 plateau in the entropy as a function of T .

As easily understood from the above explanation, the quadruple degeneracy should be lifted around at $T=\Delta E$, where ΔE denotes the first excitation energy among local low-

energy states. In fact, we observe a clear peak in the specific heat at $T \approx \Delta E$, since the entropy is changed from log 3 to log 2. The log 2 entropy originates from the double degeneracy in the local vibronic states with $J_0=\pm 1/2$, corresponding to clockwise and anti-clockwise rotational directions. Around at a temperature where the rotational moment is screened by orbital moments of conduction electrons, the entropy of log 2 is eventually released and a peak is formed in the specific heat. This peak naturally defines a characteristic temperature, which is called here the Kondo temperature T_K .

In order to confirm the relevant quantity of the present Kondo phenomenon, we investigate several kinds of susceptibilities. As shown in Fig. 3(b), we observe that susceptibilities for charge ρ , z -component of pseudospin σ_z , and total angular momentum J are rapidly suppressed in the high-temperature region. On the other hand, we observe that $\chi_{\sigma_x}=\chi_{\sigma_y}$ and they show characteristic behavior at temperatures where entropy is released. Note here that $\sigma_x=\sigma_++\sigma_-$ and $\sigma_y=-i(\sigma_+-\sigma_-)$ in the chiral bases, but they are transformed to τ_x and τ_z in the original Hamiltonian. Since Jahn-Teller distortions Q_2 and Q_3 are coupled with τ_x and τ_z , it is quite natural to find the similar characteristic behavior for the susceptibilities of Q_2 and Q_3 , as shown in Fig. 3(c). On the other hand, the susceptibility for phonon rotational moment L is rapidly decreased in the high-temperature region.

For the case without anharmonicity, we have clearly observed that the total angular momentum J , composed of pseudo spin and phonon angular momenta, is screened to form the singlet ground state of $J=0$.^{19,20} On the other hand, in the present case with strong anharmonicity, J itself is no longer a good quantum number. However, the rotational direction, clockwise or anti-clockwise, is still a relevant degree of freedom, as understood from the fact that the local ground states are characterized by $J_0=\pm 1/2$. In other words, orbital (quadrupole) degree of freedom plays a crucial role in the present Kondo phenomenon. Concerning the viewpoint of the actual detection of this Kondo phenomenon, quadrupole susceptibilities for Q_2 and Q_3 are quite important, since they are closely related to the elastic constant observed by ultrasound experiments.

In Fig. 4(a), we plot the characteristic temperatures (solid symbols) which form peaks in the specific heat for the case of $\omega=0.1$, $\alpha=1$, and $\gamma=1$. Note that in this case, in the region of $|\beta| < 1.5$, we do not find any peak temperatures in the specific heat, since the entropy is rapidly decreased to zero in the high-temperature region. For $|\beta| > 1.5$, we observe two peaks in the specific heat. As mentioned above, the higher one is characterized by the local excitation energy ΔE , while the lower one is considered as the Kondo temperature T_K . In Fig. 4(a), the solid circles are well fitted by solid curve of ΔE , which is obtained by the diagonalization of H_{loc} . We observe small deviations between solid circles and solid curve, but they are due to the effect of discrete temperature of the NRG calculation.

Note that in the case of $\omega=0.1$, the situation is in the adiabatic region and the dynamical Jahn-Teller effect is not so significant. Thus, it is difficult to obtain the formula of the Kondo temperature concerning the rotational degree of freedom of the vibronic state as a result of the dynamical Jahn-Teller effect. However, in the previous research, we have found that in the adiabatic region, the temperature dependence of the

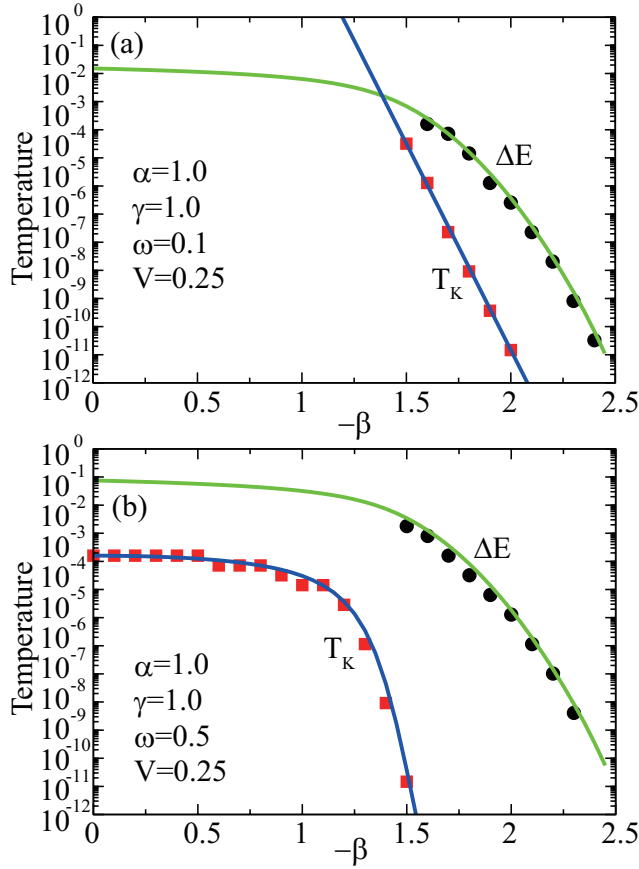


Fig. 4. Phase diagram for the Kondo effect of a Jahn-Teller vibration in a cubic anharmonic potential for (a) $\omega=0.1$ and (b) $\omega=0.5$ with $\alpha=1$ and $\gamma=1$. Solid symbols are obtained from the peak positions in the NRG results. Solid curves are drawn by the local energy ΔE and the fitting curves for T_K .

with the use of the static Jahn-Teller energy E_{JT} and appropriate parameters a and b .¹⁹⁾ When we include the anharmonicity, we have found the relation of $E_{JT} \propto |\beta|$ for fixed values of α and γ .¹⁹⁾ In fact, as shown in Fig. 4(a), we find that $\log T_K$ is in proportion to $|\beta|$ except for the value of constant shift b . This result suggests that the static Jahn-Teller energy should be relevant to the Kondo temperature in the adiabatic region.

Now we increase the value of ω in order to check the effect of adiabaticity. We do not show the NRG results of entropy, specific heat, and several kinds of susceptibilities, since we have obtained essentially the same results as Figs. 3 for the case of $\omega=0.5$. In Fig. 4(b), we plot the temperatures of the peak positions in the specific heat for $\omega=0.5$. Again we find that the higher peak temperature is well fitted by ΔE for the case of $\omega=0.5$. Note that the magnitude of ΔE becomes totally larger than that in Fig. 4(a), since ω determines the energy scale of H_{loc} . The lower peak is the Kondo temperature and in the present case, it is possible to fit the NRG results by a single curve of the Kondo temperature T_K , which is obtained from the effective s - d model, discussed below.

Let us explain the effective s - d model of the Jahn-Teller-Anderson Hamiltonian. First we distinguish the local degenerate ground states of H_{loc} as $|\pm\rangle = |\Phi_{0,\pm 1/2}^{(1)}\rangle$ and the ground-state energy is given by $E_{0,\pm 1/2}^{(1)}$. After some algebraic calculations concerning the second-order perturbation in terms of

the hybridization, we obtain the effective s - d model as

$$H_{\text{eff}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\mathbf{k}, \mathbf{k}'} [J_z (c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}'\uparrow} - c_{\mathbf{k}\downarrow}^\dagger c_{\mathbf{k}'\downarrow}) S_z + J_\perp (c_{\mathbf{k}\downarrow}^\dagger c_{\mathbf{k}'\uparrow} S_+ + c_{\mathbf{k}\uparrow}^\dagger c_{\mathbf{k}'\downarrow} S_-)], \quad (29)$$

where $S_z = (|+\rangle\langle+| - |-\rangle\langle-|)/2$, $S_+ = |+\rangle\langle-|$, $S_- = |-\rangle\langle+|$, and the exchange interactions are given by

$$J_\perp = \sum_{\mathbf{k}} \frac{2V^2 a_{\mathbf{k}}^2}{E_{\mathbf{k},0}^{(0)} - E_{0,1/2}^{(1)}}, \quad (30)$$

and

$$J_z = \sum_{\mathbf{k}} \frac{2V^2 (a_{\mathbf{k}}^2 - b_{\mathbf{k}}^2)}{E_{\mathbf{k},0}^{(0)} - E_{0,1/2}^{(1)}}. \quad (31)$$

Here $a_{\mathbf{k}}$ and $b_{\mathbf{k}}$ are given by

$$a_{\mathbf{k}} = \sum_{n,\ell} Q_{n,\ell}^{(0,1/2)} P_{n,\ell}^{(k,0)}, \quad (32)$$

and

$$b_{\mathbf{k}} = \sum_{n,\ell} R_{n,\ell}^{(0,1/2)} P_{n,\ell}^{(k,1)}, \quad (33)$$

respectively. Except for the definitions of J_\perp and J_z , the model is essentially the same as that for the harmonic Jahn-Teller phonons.²⁰⁾

Here we note that J_z is always smaller than J_\perp and it is decreased when $|\beta|$ is increased, leading to the rapid suppression of T_K as a function of $|\beta|$, as observed in Fig. 4(b). The effect of anharmonicity appears in the suppression of the z -component of the exchange interaction. This is consistent with the relation of $\chi_{\sigma_x} = \chi_{\sigma_y} > \chi_{\sigma_z}$ for $T > T_K$, since Jahn-Teller phonons are coupled with σ_+ and σ_- . The directions of the rotational Jahn-Teller modes are easily converted for high-energy Jahn-Teller phonons.

For the s - d model with anisotropic exchange interaction, the explicit expression for the binding energy \bar{E} has been already obtained.³⁹⁾ When we define the Kondo temperature T_K as $T_K = -\bar{E}$, we express T_K as

$$T_K = D \exp \left[\frac{-1}{2\rho_0 \sqrt{J_\perp^2 - J_z^2}} \tan^{-1} \left(\frac{\sqrt{J_\perp^2 - J_z^2}}{J_z} \right) \right]. \quad (34)$$

In Fig. 4(b), numerical results are shown by solid squares and the curve on the solid square denotes T_K . We find that the numerical results agree well with the analytic curve of T_K of the s - d model with the anisotropic exchange interaction.

5. Discussion and Summary

In this paper, we have discussed the Kondo phenomena due to the Jahn-Teller ion vibrating in the cubic anharmonic potential by using the numerical renormalization group method. Concerning the magnitude of the anharmonicity, we have considered the region of $|\beta| < 2.5$ in this paper, but it is possible, in principle, to perform the numerical calculations even for the region of $|\beta| > 2.5$. However, it is necessary to pay due attention to the reliability of the numerical results, since the Kondo temperature is expected to be extremely low in such a case. In fact, from the viewpoint of the limitation of the numerical calculations, it is difficult to obtain the reliable results in the present calculation, when the Kondo temperature be-

comes the order of 10^{-12} . Thus, for the case with very strong anharmonicity, it is difficult to confirm the results by actual calculations, but we expect that the curves of ΔE and T_K in Fig. 4(b) are simply extended to the lower-temperature side. Namely, we deduce that the picture of the two-step entropy release is invariant even for large $|\beta|$.

Throughout this paper, we have ignored the Coulomb interaction. As mentioned previously in the research of orbital ordering phenomena in manganites,^{40,41)} in the present spinless model, the inter-orbital Coulomb interaction effectively enhances the static Jahn-Teller energy. This is quite natural, since the Jahn-Teller distortion occurs, only when one electron is included at an impurity site and orbital degree of freedom becomes active. In fact, we simply observe the suppression of T_K , when we include the inter-orbital Coulomb interaction in the present model. Thus, we have not considered the Coulomb interaction in this paper.

However, the situation will be changed, if we consider explicitly the spin degree of freedom. In this paper, in order to focus the Kondo effect due to anharmonic Jahn-Teller vibrations, we have considered only the spinless model, but we are also interested in the competition between spin and orbital degrees of freedoms. On the basis of this viewpoint, recently, we have analyzed the two-orbital spinful Anderson model including both Coulomb interactions and the coupling between electrons and Jahn-Teller phonons on an impurity site.³³⁾ A local problem has been analyzed in detail for the confirmation of a spin-vibronic quartet ground state, which is characterized by the direct product of spin and vibronic degrees of freedom. Then, the hybridization term has been included and the model has been analyzed with the use of the NRG method. From the evaluation of entropy, specific heat, and several kinds of susceptibilities, it has been found that spin and total angular momenta are simultaneously screened by conduction electrons, leading to the Kondo phenomenon due to the entropy release of $\log 4$ of the local spin-vibronic state. It is one of future problems to clarify the effect of cubic anharmonicity on the Kondo effect due to the spin-vibronic state.

As mentioned in the last paragraph of Sec. 2.2, we have not discussed in detail the quantum phonon states for the case of $N=0$. However, it is an interesting problem to clarify the properties of eigenstates of H_{ph} . Since our interests have focused on the low-temperature properties of the Kondo phenomena in this paper, we have not remarked the peculiar properties of anharmonic Jahn-Teller vibration in the high-temperature region. This is another future problem.

In summary, we have clarified the Kondo effect in the Jahn-Teller-Anderson model with cubic anharmonicity. We have found the $\log 3$ plateau in the entropy due to quasi-triple degeneracy in the low-energy states including vibronic ground states. With the further decrease of temperature, we have observed the region of $\log 2$ plateau due to the vibronic state with rotational degree of freedom. The rotational moment of the vibronic state has been found to be suppressed by the screening of orbital moments of conduction electrons, leading to the Kondo effect. It has been shown that T_K is well explained by the effective s - d model with anisotropic exchange interactions.

Acknowledgement

The author is grateful to K. Ueda for fruitful discussions concerning the Kondo phenomena. He also thanks Y. Aoki, T. D. Matsuda, R. Higashinaka, and A. Shudo for discussions on rattling in cage-structure materials. This work has been supported by a Grant-in-Aid for Scientific Research (C) (No. 24540379) of Japan Society for the Promotion of Science. The computation in this work has been partly done using the facilities of the Supercomputer Center of Institute for Solid State Physics, University of Tokyo.

- 1) *Proc. Int. Conf. Heavy Electrons (ICHE2010)*, J. Phys. Soc. Jpn. **80** (2010) Suppl. A.
- 2) *Advances in Physics of Strongly Correlated Electron Systems*, J. Phys. Soc. Jpn. **83** (2014) 061001-061019.
- 3) Kondo effect and its related phenomena have been reviewed in J. Phys. Soc. Jpn. **74** (2005) 1-238.
- 4) J. Kondo: *Physica B+C* **84** (1976) 40.
- 5) J. Kondo: *Physica B+C* **84** (1976) 207.
- 6) K. Vladár and A. Zawadowski: *Phys. Rev. B* **28** (1983) 1564.
- 7) K. Vladár and A. Zawadowski: *Phys. Rev. B* **28** (1983) 1582.
- 8) K. Vladár and A. Zawadowski: *Phys. Rev. B* **28** (1983) 1596.
- 9) C. C. Yu and P. W. Anderson: *Phys. Rev. B* **29** (1984) 6165.
- 10) T. Matsuura and K. Miyake: *J. Phys. Soc. Jpn.* **55** (1986) 29.
- 11) T. Matsuura and K. Miyake: *J. Phys. Soc. Jpn.* **55** (1986) 610.
- 12) H. Sato, H. Sugawara, Y. Aoki, and H. Harima: *Handbook of Magnetic Materials* Volume 18, ed. K. H. J. Buschow, pp. 1-110, Elsevier, Amsterdam, 2009.
- 13) S. Sanada, Y. Aoki, H. Aoki, A. Tsuchiya, D. Kikuchi, H. Sugawara, and H. Sato: *J. Phys. Soc. Jpn.* **74** (2005) 246.
- 14) S. Yotsushashi, M. Kojima, H. Kusunose, and K. Miyake: *J. Phys. Soc. Jpn.* **74** (2005) 49.
- 15) K. Hattori, Y. Hirayama, and K. Miyake: *J. Phys. Soc. Jpn.* **74** (2005) 3306.
- 16) K. Hattori, Y. Hirayama, and K. Miyake: *J. Phys. Soc. Jpn.* **75** (2006) Suppl. 238.
- 17) K. Mitsumoto and Y. Ōno: *Physica B* **403** (2008) 859.
- 18) K. Mitsumoto and Y. Ōno: *J. Phys. Soc. Jpn.* **79** (2010) 054707.
- 19) T. Hotta: *Phys. Rev. Lett.* **96** (2006) 197201.
- 20) T. Hotta: *J. Phys. Soc. Jpn.* **76** (2007) 023705.
- 21) T. Hotta: *J. Phys. Soc. Jpn.* **76** (2007) 084702.
- 22) T. Hotta: *Physica B* **403** (2008) 1371.
- 23) T. Hotta: *J. Phys. Soc. Jpn.* **77** (2008) 103711.
- 24) T. Hotta: *J. Phys. Soc. Jpn.* **78** (2009) 073707.
- 25) S. Yashiki, S. Kirino, and K. Ueda: *J. Phys. Soc. Jpn.* **79** (2010) 093707.
- 26) S. Yashiki, S. Kirino, K. Hattori, and K. Ueda: *J. Phys. Soc. Jpn.* **80** (2011) 064701.
- 27) S. Yashiki and K. Ueda: *J. Phys. Soc. Jpn.* **80** (2011) 084717.
- 28) K. Hattori: *Phys. Rev. B* **85** (2012) 214411.
- 29) T. Hotta and K. Ueda: *Phys. Rev. Lett.* **108** (2012) 247214.
- 30) T. Fuse and Y. Ōno: *J. Phys. Soc. Jpn.* **79** (2010) 093702.
- 31) T. Fuse and Y. Ōno: *J. Phys. Soc. Jpn.* **80** (2011) SA136.
- 32) T. Fuse, Y. Ōno, and T. Hotta: *J. Phys. Soc. Jpn.* **81** (2012) 044701.
- 33) T. Fuse and T. Hotta: *J. Phys.: Conf. Ser.* **428** (2013) 012013.
- 34) T. Fuse and T. Hotta: *J. Korean Phys. Soc.* **62** (2013) 1874.
- 35) T. Fuse and T. Hotta: To appear in the Proceedings of SCES2013.
- 36) Y. Takada: *Phys. Rev. B* **61** (2000) 8631.
- 37) K. G. Wilson: *Rev. Mod. Phys.* **47** (1975) 773.
- 38) H. R. Krishna-murthy, J. W. Wilkins, and K. G. Wilson, *Phys. Rev. B* **21** (1980) 1003.
- 39) H. Shiba: *Prog. Theor. Phys.* **43** (1970) 601.
- 40) E. Dagotto, T. Hotta, and A. Moreo: *Phys. Rep.* **344** (2001) 1.
- 41) T. Hotta: *Rep. Prog. Phys.* **69** (2006) 2061.